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IODIC ACID PROCESS FOR THE DETERMINA-
TION OF BROMINE IN HALOGEN SALTS.

By F. A. GOOCH and P. L. BLUMENTHAL.

(Contributions from the Kent Chemical Laboratory, Yale
University, New Haven, Conn., U. S. A.)

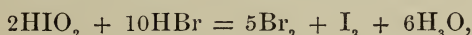
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ART. XLI.—*The Iodic Acid Process for the Determination of Bromine in Halogen Salts*; by F. A. GOOCH and P. L. BLUMENTHAL.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxxxvi.]

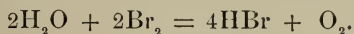
THE oxidation potential of a solution of chlorine in potassium chloride and water is, according to Bancroft,* about 0.241 volt higher than that of a solution of bromine in potassium bromide and water. Iodic acid has an oxidation potential 0.064 volt higher than that of an equivalent and equally acidified bromine solution. The consideration of these oxidation potentials suggested to Bugarsky† the choice of iodic acid as an oxidizer for the liberation of bromine from mixtures containing a bromide and a chloride.

Bugarsky's method of separating the bromine from such a mixture consists in adding sulphuric acid with a known amount of potassium diiodate, and boiling. The bromine and the iodine which are liberated in the interaction of the free acids, according to the equation



escape from the solution and may be collected in the distillate. These free halogens may be made the measure of the bromide taken, or the amount of the bromide may be calculated from the amount of the iodic acid remaining. When the liberated halogens are absorbed in potassium iodide, the amount of free iodine, as determined by titration, proves to be much less than is to be expected from the equation above, and Bugarsky, convinced that the results are much more nearly in accord with the theory when the excess of the iodic acid remaining is made the measure of the reaction, prefers, therefore, to estimate the bromide by determining in an aliquot portion of the boiled solution the iodate which remains, and to determine the chloride in another aliquot portion of the solution by Volhard's process of titration with standard sulphocyanate.

The difference in the results of these two methods of determination Bugarsky attributes to loss of free bromine by the action of steam, in consequence of which hydrobromic acid is formed and oxygen set free, as in the equation



But Andrews points out that hydrobromic acid thus formed, if returned with the condensed steam to the liquid, must be reox-

*Zeitschr. phys. Chem., x, 405.

†Zeitschr. anorg. Chem., x, 387.

idized by more iodic acid, with the result that the bromine determination by calculation from the amount of iodic acid remaining will be high rather than low. Andrews' results for bromine were high to the extent of 1 per cent to 1.5 per cent. The differences in experience and view of these investigators have led us to further investigation of the reaction.

Suitable solutions of sodium chloride and potassium bromide* were prepared and standardized gravimetrically by silver precipitation. An iodine solution, approximately N/10, standardized against N/10 arsenite, and N/10 sodium thiosulphate, standardized against the iodine solution, were used. Finally, a solution of potassium iodate† (3.5670 grams per liter) was prepared, and its iodine value was determined by titrating with the thiosulphate the iodine liberated from 50^{cm}³ portions by the action of potassium iodide in presence of sulphuric acid. To avoid errors of titration due to an indefinite end point, the gravimetric determination of chlorine was substituted for the Volhard process. Gaseous nitrogen trioxide, liberated from sodium nitrite and washed by nitric acid, was used instead of the sodium nitrite or potassium nitrite used by Bugarsky.

The method of carrying out determinations was as follows: To 50^{cm}³ of the solution, containing known amounts of sodium chloride and potassium bromide, 50^{cm}³ of the iodide solution of known value and 10^{cm}³ of 20 per cent sulphuric acid were added and the solution was diluted to 200^{cm}³, in a 500^{cm}³ Erlenmeyer flask. A few bits of platinum foil were added, to prevent bumping, and the solution was boiled down to about 80^{cm}³, some 30 minutes being required. After cooling, the solution was transferred to a carefully calibrated 100^{cm}³ flask and made up to the mark.

Half the solution was pipetted into an Erlenmeyer flask fitted with an inverted mushroom trap, through which potassium iodide was added. The liberated iodine was titrated with thiosulphate, and 1/6 of it was taken as the equivalent of the excess iodate in the portion.

The remaining half of the solution was transferred to a beaker, the flask and stopper being carefully rinsed, and an excess of gaseous sulphur dioxide (vaporized from the liquid) was passed in. Gaseous nitrogen trioxide (liberated from sodium nitrite or potassium nitrite by nitric acid, and washed by the same) was passed into the solution to destroy the excess of sulphur dioxide acid and to liberate the iodine.‡ The solution was boiled until free from iodine, and the chlorine of the resid-

* The "analyzed" C. P. article, free from chloride, so far as could be determined by qualitative tests, (this Journal (3), xl, 289).

† KIO₃.

‡ The nitrogen trioxide prepared in the manner described produced no turbidity in a solution of silver nitrate acidulated with nitric acid.

ual chloride was precipitated by silver nitrate. After standing over night, the silver chloride was filtered off on asbestos in a perforated crucible, dried at gentle heat, and weighed.

The amounts of potassium bromide calculated from the iodate used up, and the amounts of sodium chloride equivalent to the silver chloride weighed, are given in the table, in comparison with the amounts taken of these substances respectively.

Molecular Ratio of KBr to NaCl, 1:1.

KBr taken. gram.	NaCl taken. gram.	KBr. formed. gram	NaCl formed. gram.	Error in KBr. gram.	Error in NaCl. gram.	Final volume. cm ³ .
0.1984	0.0974	0.2006	0.0995	+0.0022	+0.0021	*
0.1984	0.0974	0.1981	0.0996	-0.0003	+0.0022	*
0.1984	0.0974	0.1996	0.1003	+0.0012	+0.0029	*
0.1984	0.0974	0.1983	0.0996	-0.0001	+0.0022	*
0.1984	0.0974	0.1939	0.1004	-0.0045	+0.0030	76
0.1984	0.0974	0.1966	0.1008	-0.0018	+0.0034	74
0.1984	0.0974	0.1990	0.0998	+0.0006	+0.0024	38
0.1984	0.0974	1.1945	0.1004	-0.0039	-0.0030	74

* The final volume, 50^{cm}³ to 75^{cm}³, was not measured exactly.

Molecular Ratio of KBr to NaCl, 2:1.

0.1984	0.0487	0.1940	0.0517	-0.0044	+0.0030	50
0.1984	0.0487	0.1904	----	-0.0080	----	65
9.1984	0.0487	0.1926	0.1519	-0.0058	+0.0032	68
0.1984	0.0487	0.1965	0.0522	-0.0019	+0.0035	65
0.1984	0.0487	0.1942	----	-0.0042	----	78
0.1984	0.0487	0.1945	0.0521	-0.0039	+0.0034	80
0.1984	0.0487	0.1949	0.0518	-0.0035	+0.0031	65
0.1984	0.0487	0.1942	0.0526	-0.0042	+0.0039	70
0.1984	0.0487	0.1959	0.0525	-0.0025	+0.0038	76

Molecular Ratio of KBr; NaCl, 1:2.

0.1984	0.1948	0.1964	0.1954	-0.0020	+0.0006	*
0.1984	0.1948	0.1952	0.1990	-0.0032	+0.0042	*
0.1984	0.1948	0.1967	0.1969	-0.0017	+0.0021	*
0.1984	0.1948	0.1978	0.1984	-0.0006	+0.0036	*
0.1984	0.1948	0.1974	0.1980	-0.0010	+0.0032	*
0.1984	0.1948	0.1983	0.1984	-0.0001	+0.0036	*
0.1984	0.1948	0.1988	0.1985	+0.0004	+0.0037	*
0.1984	0.1974	0.1983	0.1028	-0.0001	+0.0054	75
0.1984	0.1974	0.1960	0.1022	+0.0024	+0.0048	70

* The final volume, 50^{cm}³ to 75^{cm}³, was not measured exactly.

In these experiments, made with reagents carefully standardized at the outset and restandardized in the course of the investigation, the errors are generally large and irregular, independent of the final concentrations within the limits shown,

and out of all proportion to any possible chloride contamination of the standard bromide. The fact that the chlorine proves to be invariably high and the bromine generally low, suggests the probability that the iodic acid reaction fails to remove all the bromine in the process of boiling.

Bromine was found in the silver chloride obtained from the combined residues of several determinations by applying the chloroform test to the water extract of the sodium carbonate fusion of these residues, after acidulating with sulphuric acid and adding a drop or two of chlorine water. Furthermore, in a special experiment in which pure potassium bromide was treated according to the procedure outlined, the titration figures of the excess of iodate corresponded to only 0.1945 gm. of potassium bromide out of 0.1984 gm. taken; while, after treatment with sulphur dioxide followed by nitrogen trioxide, and boiling until all iodine had been expelled (as shown by the starch test applied to the cool solution), silver nitrate precipitated from the solution silver bromide equivalent to 0.0036 gm. of potassium bromide. The 0.1945 gm. of the potassium bromide indicated by the determination of the iodate and the 0.0036 gm. equivalent to the silver bromide precipitated after reduction make up 0.1981 gm. of the 0.1984 gm. taken. In this experiment, therefore, the deficiency of bromine and the excess of chlorine noted were plainly due to the retention of bromine, after the iodic acid treatment, in some combination such that the process of reducing the residual iodic acid and expelling the iodine left it in condition to be precipitated as silver bromide, which was counted as silver chloride.

The combination of iodine with bromine in this experiment and of iodine with bromine and chlorine in the experiments of the table, would account for the observed deficiencies in bromine and excess in chlorine; and a little consideration shows that the conditions of the process are favorable to the formation of such combinations. Thus free bromine and free iodine, both products of the main reaction, may readily combine to form iodine monobromide,



Furthermore, Roberts* has shown that iodic acid, iodine, and aqueous hydrochloric acid react to form iodine monochloride, according to the reaction



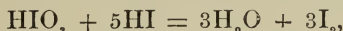
and it may reasonably be expected that in the reaction of iodic acid and hydrobromic acid in presence of free iodine (pro-

* This Journal (3), xlviii, 1, 58.

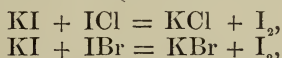
duced in the main reaction, previously cited) iodine monobromide will be similarly formed, according to the equation



When the acidulated solution containing an excess of iodic acid with more or less iodine monochloride, or monobromide, is treated with potassium iodide for the purpose of determining the excess of iodic acid by means of the iodine liberated,



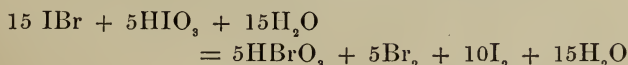
the iodine compounds of the halogens will contribute to the amount of the free iodine which measures the iodic acid,



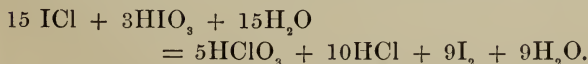
and this increase in free iodine will produce a corresponding deficiency in the bromide, which is estimated from the amount of iodate which has disappeared.

When, on the other hand, the excess of iodate is reduced by sulphur dioxide preparatory to determining the chloride, the iodine monochloride is converted to hydriodic acid and hydrochloric acid, and the iodine monobromide to hydriodic acid and hydrobromic acid. The hydriodic acid is destroyed, and the iodine removed, in the subsequent treatment with nitrogen trioxide; the hydrochloric acid is regularly estimated as silver chloride; but the hydrobromic acid remains to produce silver bromide, which contaminates the silver chloride and causes an error of excess in the chloride determination.

These hypothetical effects are in precise accordance with the observed phenomena. It is conceivable, and even probable, that chloric acid and bromic acid may appear also as products of the hydrolysis of the halogen compounds in presence of water and iodic acid. Thus the hydrolysis of iodine monobromide may proceed according to the expression



and that of iodine monochloride according to the equation



The production of bromic acid by hydrolysis of iodine bromide, with elimination of the free halogens and substitution of bromic acid for an equivalent amount of iodic acid, will tend to reduce the tendency to negative errors in the determination of bromine; but the bromine of the bromic acid will still be

capable of contaminating the silver chloride precipitated by silver nitrate after reduction.

The effect of chloric acid substituted for iodic acid will depend upon the conditions of concentration. So far as it may act as an oxidizer in the treatment of potassium iodide, it will tend to produce a positive error in the determination of bromine. So far as it escapes reduction in the treatment of sulphur dioxide and nitrogen trioxide, it will tend to produce an error of deficiency in the determination of chlorine.

The extent to which these various possibilities may influence results will depend upon the conditions of action and possible balancing of errors. The experimental results given above show plainly that under the conditions defined the separation of bromine from chlorine in halogen salts by the action of iodic acid, though based upon a reaction ideal in respect to the relation of the oxidation potentials, is vitiated by secondary effects. These effects may be reasonably attributed to the action of small amounts of iodine monochloride and iodine monobromide formed in the interaction of iodic acid and free iodine with hydrochloric acid and hydrobromic acid, or to the action of chloric acid and bromic acid derived from iodine monochloride or bromine monochloride by hydrolysis.



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